DECAY OF ENDOSULFAN (THIODAN) RESIDUE ON LEAVES OF STRAWBERRY PLANTS IN MONTEREY COUNTY, CALIFORNIA - APRIL 1976

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INTRODUCTION

Endosulfan (Thiodan) is a highly toxic chlorinated hydrocarbon used as an insecticide - acaracide. This material is registered to control a wide variety of insects, including aphids, mites, cutworms and thrips, on citrus and small fruits, vegetables, forage crops, oil crops, fiber crops, grains, tobacco, coffee, tea and ornamentals. Its major use is on lettuce and tomatoes, but over 12,514 pounds of endosulfan were applied to more than 6,076 acres of strawberries in 1975.

The acute oral LD_{50} (rat) is 30 mg/kg in alcohol suspension, 70 mg/kg in aqueous suspension, and 110 mg/kg in oil. The dermal LD_{50} (rabbit) is 395 mg/kg. This chemical is a central nervous system stimulant.

Technical endosulfan is a mixture of two isomers, endosulfan I and II. Endosulfan I is in greater abundance than its isomer prior to application. After application, the parent compound begins to isomerize so that approximately equal amounts of I and II are in residues. Endosulfan III is a degradation product of both parent isomers and occurs as a result of plant metabolism. Endosulfan III has a lower toxicity than the parent compounds, but is more persistent. Label directions for Thiodan 2MS Emulsive (Soil-Serv) allow dosage rates for strawberries of up to 8 quarts per acre on the U. S. West Coast. The preharvest interval for Thiodan on strawberries is 4 days with a tolerance of 2 ppm.

APPLICATION

The study of the decay of endosulfan on strawberries in Monterey County began two weeks before harvest and ran until harvest time. Application was made at the rate of 300 gallons per acre volume. The chemicals applied were Thiodan 2MS (SoilServ) 2 gallons (4 pounds) per acre; Kelthane 1 quart/acre and glycol buffer 1 pint per 100 gallons.

SAMPLING

Leaves of the strawberry plant that workers come into contact with were sampled with a leaf punch at intervals beginning three hours after application. Triplicate samples were taken at every interval each consisting of about 100 leaf discs, 2.5 cm in diameter. They were analyzed for dislodgeable, penetrated and total residue of the two isomers of endosulfan and the sulfate. The samples were placed on ice for transportation to the laboratory.

ANALYTICAL PROCEDURES

Extraction:

The sample container and leaf punches are weighed and the gross weight recorded.

Total Residues

1. The leaf punches are transferred to a blending jar. The empty sample container is again weighed and the net weight of the punches recorded.

2. Approximately 100 gms (approx. 50 mls) of sodium sulfate and 100 mls of benzene are added.

3. The sample is blended at high speed for 3 minutes, keeping the blender cup cool by immersing it in a container of cool water. The blender cup is removed and the sample allowed to settle.

4. An aliquot is decanted into a teflon-capped bottle and stored in the freezer prior to clean up and analysis.

Dislodgeable Residues

1. Fifty mls of water and approximately 4 drops of Sur-Ten solution (1:50) is added to the sample container. The container is capped and placed in a multi-purpose rotator and rotated at 30 cycles/min. for 60 min. The aqueous solution is decanted through a glass wool plug into a 500 ml separatory funnel.

2. The punches are rotated a second time, using 50 mls of water and 4 drops of Sur-Ten solution, for 30 min. This is added to the first extraction.

3. The sample is then hand-shaken for approximately 10 secs with 30 mls of water. The container is drained into the separatory funnel with the first two extractions.

4. The aqueous solution is extracted three times with 50 ml of cyclohexene. The extract is filtered through sodium sulfate into a glass stoppered mixing cylinder and the volume is recorded. The extract is mixed in the cylinder. An aliquot is decanted into a teflon-capped bottle and stored in the freezer prior to clean up and analysis.

Penetrated Residue

1. After the last water rinse is drained for the dislodgeable residue, the punches are transferred to a blender jar. The empty sample container is weighed and the net weight of the punches recorded.

2. Approximately 100 gms (approximately 50 mls) of sodium sulfate and 100 mls of benzene are added.

3. The sample is blended and handled the same as the total residue sample.

GLC Analysis Conditions

Varian 2700, Electron Capture Detector
6' x 2 mm of 3% OV-101 220°, 30 cc/min N_2 carrier

Optional column:
6' x 2 mm of 1.5% OV-17/ 2% OV-210 225°, 30 cc/min
N_2 carrier

Retention Times--OV-17/OV-210 column

Thiodan I	2 min
Thiodan II	3 min
Thiodan III	4 min

Recoveries:
Recoveries of all three compounds were in excess of 95% of theoretical.

RESULTS

Daily weather observations made at Salinas over the study period are recorded in Table 1. The average maximum and minimum temperatures were 66.0 and 44.6°F., respectively. There were trace amounts of rain recorded during the study.

Dislodgeable, penetrated and total residue values are given in Table 2 and on Graph 1. Surface residues of both isomers were below 2 ppm after 6 days. Surface residues of the oxidation produce never got above 0.27 ppm. Penetrated residues of the parent compound were much higher than dislodgeable residues and decreased steadily for 9 days at which time the levels were below 10 ppm. The oxidation product of the penetrated compound increased slowly throughout the study to approximately 14 ppm.

TABLE I

DAILY TEMPERATURE AND PRECIPITATION

Observations made at Salinas in Monterey County, California

Date (1976)	Temperature (°F) Maximum	Minimum	Precipitation (inches) (24 hour amount observation)
4/13	61	47	Trace
4/14	64	50	Trace
4/15	55	42	.07
4/16	61	39	
4/17	59	38	Trace
4/18	65	48	Trace
4/19	73	43	
4/20	61	49	
4/21	64	48	
4/22	70	50	
4/23	75	47	
4/24	67	44	
4/25	71	42	
4/26	70	39	
4/27	63	47	
4/28	68	41	
4/29	75	44	
Average	66.0	44.6	Total 0.07

TABLE 2

RESIDUE ON STRAWBERRY LEAVES
FOLLOWING THIODAN APPLICATION

Date	Sample	Surface Residue (PPM)			Penetrated Residue (PPM)			Total Residue (PPM)		
		I	II	III	I	II	III	I	II	III
(hours)										
4/13 (1100)	1	15.7	9.7	.10	330.0	166.0	2.39			
4/13 (1100)	2	10.1	6.7	.04	314.0	166.0	1.72			
4/13 (1100)	3							192.0	114.0	3.32
4/13 (1600)	4	6.46	5.60	.08	260.0	152.0	3.38			
4/13 (1600)	5	3.0	2.4	.04	175.0	105.0	1.58			
4/13 (1600)	6							186.0	111.0	4.58
April 14	7	3.0	3.39	.09	185.0	123.0	4.94			
April 14	8	3.63	4.44	.37	143.0	128.0	4.56			
April 14	9							344.0	119.0	5.04
April 16	10	1.56	2.19	.08	96.1	92.2	4.19			
April 16	11	3.93	5.02	.25	105.0	95.7	4.79			
April 16	12							94.2	93.3	4.25
April 20	13	.17	.33	.05	30.8	42.8	3.83			
April 20	14	.46	.92	.09	39.2	40.9	5.42			
April 20	15							18.6	39.8	.39
April 22	16	.12	.22	.05	4.13	7.26	4.95			
April 22	17	.23	.53	.10	6.01	11.74	9.67			
April 22	18							6.71	12.73	9.61
April 27	19	.10	.22	.14	8.5	12.5	8.51			
April 27	20	.14	.32	.21	26.12	38.54	10.99			
April 27	21							14.07	21.34	11.48
April 29	22	.12	.32	.18	7.06	13.8	16.68			
April 29	23	.06	.16	.06	8.83	16.06	12.84			
April 29	24							12.84	23.25	19.84

GRAPH 1: THIODAN RESIDUE DECAY ON STRAWBERRY LEAVES (PPM)